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(54) **Modified conjugated diene polymer and process for production thereof.**

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Rubber Chemistry and Technology, vol 58,
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Description

This invention relates to a novel process for producing a modified conjugated diene polymer having excellent wear resistance and excellent mechanical characteristics, by polymerizing a conjugated diene with a lanthanum series rare earth metal catalyst and reacting the resulting reactive polymer with a specific compound. This invention further relates to a novel modified conjugated diene polymer produced according to said process.

In recent years, requirements of higher durability and longer life for component rubbers are increasing. Hence, it has become necessary to improve rubbers in such characteristics as wear resistance, mechanical properties, heat generation

Polybutadienes (rubbery polymer) obtained using a catalyst composed mainly of nickel, cobalt, titanium, etc. have been poor in wear resistance.

Meanwhile, known rubbery polymers having excellent wear resistance are polybutadienes produced using a lanthanum series rare earth metal catalyst. Of these polybutadienes, one produced using a lanthanum series rare earth metal catalyst proposed by the present inventors in Japanese Patent Application Kokai (Laid-Open) No. 57410/1983 has particularly excellent wear resistance.

Japanese Patent Application Kokai (Laid-Open) No. 40109/1985 describes that the reaction between (a) a polybutadiene produced using a lanthanum series rare earth metal catalyst and (b) a tetrahalomethane alone or in admixture with a specific organoaluminum compound enables production of a polybutadiene with an improved processability.

However, these polybutadienes are yet insufficient to wear resistance.

This invention has been accomplished in order to solve the above-mentioned problems of the conventional techniques. This invention aims at providing a process for producing a modified conjugated diene polymer satisfying all of wear resistance, mechanical characteristics and low heat generation, as well as the modified conjugated diene polymer produced by said process.

Other objects and advantages of this invention will become apparent from the following description and accompanying drawings. In the accompanying drawings, Fig. 1 illustrates an example of the method for preparing the catalyst used in this invention.

According to this invention, there is provided a process for producing a modified conjugated diene polymer which comprises the steps of (I) polymerizing a conjugated diene in an inert solvent in the presence of a catalyst comprising (a) a lanthanum series rare earth metal compound, (b) an organoaluminum compound represented by the general formula, $A1R^1R^2R^3$ (wherein R^1 , R^2 and R^3 , which may be same or different, are hydrogen atoms or hydrocarbon groups with 1 to 8 carbon atoms and at least one of R^1 , R^2 and R^3 is said hydrocarbon group) and, if necessary, (c) a Lewis acid and/or (d) a Lewis base and (II) modifying the resulting reactive polymer with at least one modifying compound which is: (e) an organometal halide compound represented by the general formula, $R_n^4 MX_{4-n}$ (wherein R^4 is an alkyl group of 1 to 20 carbon atoms or an aryl group, M is a tin or germanium atom, X is a halogen atom, and n is an integer from 1 to 3).

This invention further provides the modified conjugated diene polymer thus produced.

According to this invention, various characteristics such as wear resistance, low heat generation, mechanical characteristics of a conjugated diene polymer, for example, polybutadiene can be improved by reacting a reactive polymer just produced by polymerizing a conjugated diene using a lanthanum series rare earth metal catalyst, with a specific compound.

The lanthanum series rare earth metal catalyst used in this invention is a catalyst system comprising (a) a lanthanum series rare earth metal compound [hereinafter referred to as the component (a)] and (b) an organoaluminum compound represented by the general formula, $A1R^1R^2R^3$ [hereinafter referred to as the component (b)]. This catalyst system can further comprise, if necessary, (c) a Lewis acid [hereinafter referred to as the component (c)] and/or (d) a Lewis base [hereinafter referred to as the component (d)].

As the lanthanum series rare earth metal compound which is the component (a), there can be preferably used compounds represented by the general formula, LnY^2_3 . Here, Ln is a lanthanum series rare earth element having an atomic number of 57 to 71 in the Periodic Table, and

cerium, lanthanum, praseodymium, neodymium and gadolinium are preferred. Of these, neodymium is particularly preferred because of its easy commercial availability. These rare earth elements may be used alone or in admixture of at least two.

Y^2 is a hydrocarbon residue, an alkoxide residue, a thioalkoxide residue, an amide residue, a phosphoric acid salt residue, a phosphorous acid salt residue, a halide residue or a carboxylic acid salt residue. Of these, an alkoxide residue, a halide residue and a carboxylic acid salt residue are particularly

preferred.

The hydrocarbon type compound of lanthanum series rare earth element includes compounds represented by the general formula, LnR_3 (wherein R is a hydrocarbon group of 1 to 20 carbon atoms, such as a benzyl group, a phenyl group, a butyl group, or a cyclopentadienyl group).

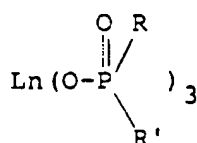
5 The alcohol type compound (alkoxide) includes compounds represented by the general formula, $\text{Ln}(\text{OR})_3$ (wherein Ln and R have the same definitions as given previously). Preferred as the alcohol are 2-ethylhexyl alcohol, oleyl alcohol, stearyl alcohol, phenol, and benzyl alcohol.

The thioalcohol type compound (thioalkoxide) includes compounds represented by the general formula, $\text{Ln}(\text{SR})_3$ (wherein Ln and R have the same definitions as given previously). Preferred as the thioalcohol is thiophenol.

10 The amide type compound (amide) includes compounds represented by the general formula, $\text{Ln}(\text{NR}_2)_3$ (wherein Ln and R have the same definitions as given previously). Preferred as the amine are dihexylamine and dioctylamine.

The phosphoric acid salt of rare earth element includes compounds represented by the general formula,

15



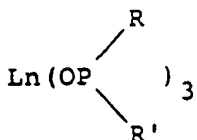
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(wherein Ln has the same definition as given previously, and R and R' may be the same or different, R' has the same definition as that of R mentioned above). Preferred as the salt are neodymium tris(diethyl phosphate) and neodymium tris(diphenyl phosphate).

25

The phosphorous acid salt of rare earth element includes compounds represented by the general formula,

30



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(wherein Ln, R and R' have the same definitions as given previously). Preferred as the salt are neodymium tris(diethyl phosphite) and neodymium tris(di(ethylhexyl) phosphite).

The halide type compound includes compounds represented by the general formula, LnX_3 (wherein Ln has the same definition as given previously and X is a halogen atom). Preferred as the halogen atom are chlorine, bromine and iodine atoms.

40

The carboxylic acid salt of rare earth element includes compounds represented by the general formula, $(\text{RCOO})_3\text{Ln}$ (wherein R is a hydrocarbon group of 1 to 20 carbon atoms, preferably a saturated or unsaturated alkyl group of straight, branched or cyclic chain, and the carboxyl group bonds to a primary, secondary or tertiary carbon atom). Preferred as the carboxylic acid are octanoic acid, 2-ethylhexanoic acid, oleic acid, stearic acid, benzoic acid and naphthenic acid.

45

Specific examples of component (a) include neodymium trichloride, didymium trichloride (didymium is a rare earth metal mixture consisting of 72% by weight of neodymium, 20% by weight of lanthanum and 8% by weight of praseodymium), neodymium 2-ethylhexanoate, didymium 2-ethylhexanoate, neodymium naphthenate, neodymium 2,2-diethylhexanoate, neodymium trimethacrylate and polymers of neodymium trimethacrylate.

50

The organoaluminum compound which is the component (b) is a compound represented by the general formula, $\text{AlR}^1\text{R}^2\text{R}^3$ (wherein R^1 , R^2 and R^3 , which may be the same or different, are hydrogen atoms or hydrocarbon groups of 1 to 8 carbon atoms, and at least one of them is said hydrocarbon group). Specific examples of the component (b) include trimethylaluminum, triethylaluminum, triisopropylaluminum, tributylaluminum, triisobutylaluminum, trihexylaluminum, tricyclohexylaluminum, diisobutylaluminum hydride, diethylaluminum hydride, dipropylaluminum hydride, ethylaluminum dihydride, propylaluminum dihydride and isobutylaluminum dihydride.

55

The Lewis acid which is the component (c) includes, for example, aluminum halide compounds represented by the general formula, $AlR^5_mS_{3-m}$ (wherein R^5 is a hydrocarbon group of 1 to 8 carbon atoms, m is 0 or a positive number of 1 to 3, and X is a halogen atom), halogen atoms, and halides of tin, titanium and the like.

Of these, particularly preferred are dimethylaluminum chloride, diethylaluminum chloride, dibutylaluminum chloride, ethylaluminum sesquichloride, ethylaluminum dichloride, and bromides and iodides corresponding to them.

The Lewis base which is the component (d) includes acetylacetone, tetrahydrofuran, pyridine, N,N-dimethylformamide, thiophene, diphenyl ether, triethylamine, organic phosphorous compounds and mono- or dihydric alcohols.

The lanthanum series rare earth metal catalyst used in this invention has the following conditions:

The mole ratio of the component (b)/the component (a) is preferably from 10 to 150, more preferably from 15 to 100. When the ratio is smaller than 10, the catalyst has a low polymerization activity. When the ratio is more than 150, the polymerization activity is not any more increased and such a high mole ratio is disadvantageous economically.

The mole ratio of the component (c)/the component (a) is preferably from 0 to 6, more preferably from 0.5 to 5.0. When the ratio exceeds 6, the polymerization activity tends to decrease.

The mole ratio of the component (d)/the component (a) is preferably from 0 to 20, more preferably from 1 to 15. When the ratio exceeds 20, the polymerization activity tends to decrease.

If necessary, the catalyst of this invention may further comprise, in addition to the components (a), (b), (c) and (d), a conjugated diene in an amount of 0 to 50 moles per mole of the lanthanum series rare earth metal compound which is the component (a). The conjugated diene used in preparation of the catalyst is the same as the monomer used in polymerization and may be isoprene, 1,3-butadiene, or 1,3-pentadiene. The conjugated diene as a catalyst component is not essential, but its use in the catalyst can noticeably enhance the activity of the catalyst.

The preparation of the catalyst if conducted, for example, by subjecting the components (a) to (d) dissolved in a solvent and, if necessary, the conjugated diene to reaction. In this case, the addition order of each component is not critical. It is preferable to previously mix these components and subject the mixture to reaction and aging from the standpoints of enhancement of polymerization activity and shortening the induction period for polymerization initiation. It is also possible to successively add the catalyst components directly to a mixture of a polymerization solvent and a monomer to be polymerized, during the polymerization.

An example of the preparation method of the catalyst used in this invention is illustrated in Fig.1. As shown in Fig. 1, the lanthanum series rare earth metal catalyst used in this invention consists of (A) a lanthanum series rare earth metal compound (a) which is a transition metal component, (B) an organoaluminum compound (b) which is an organometal component, and, if necessary, (C) a Lewis acid (c) and/or a Lewis base (d), both of which are a third component, and the addition order of these components (a) to (d) in the preparation of the catalyst is not critical.

In the catalyst preparation, it is preferable to contact the component (a) with the component (d), though the addition order of the other components is not critical.

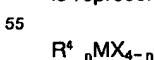
The polymerization solvent is an inert organic solvent. It includes aromatic hydrocarbons such as benzene, toluene and xylene; aliphatic hydrocarbons such as n-pentane, n-hexane, n-butane and cyclohexane; alicyclic hydrocarbons such as methylcyclopentane and cyclohexane; and halogenated hydrocarbons such as ethylene dichloride and chlorobenzene. These solvents can be used alone or in admixture of two or more.

The polymerization temperature is preferably -20°C to 150°C , more preferably 30° to 120°C . The polymerization reaction can be conducted batchwise or continuously.

The monomer concentration in the polymerization solvent is preferably 5 to 50% by weight, more preferably 10 to 35% by weight.

In order for the lanthanum series rare earth metal catalyst and the formed polymer not to lose their activity during the polymerization, attention should be paid so that substances having a deactivating effect, such as oxygen, water and carbon dioxide cannot be introduced into the polymerization system.

In this invention, the organometal halide compound (e) to be allowed to react with the reactive polymer is represented by the general formula:



wherein R^4 is an alkyl group of 1 to 20 carbon atoms or an aryl group, M is a tin or germanium atom, X is a

halogen atom, and n is an integer of 1 to 3.

When M is a tin atom, the component (e) is, for example, triphenyltin chloride, tributyltin chloride, triisopropyltin chloride, diphenyltin dichloride, dioctyltin dichloride, dibutyltin dichloride, phenyltin trichloride or butyltin trichloride.

5 When M is a germanium atom, the component (e) is, for example, triphenylgermanium chloride, dibutylgermanium dichloride, diphenylgermanium dichloride, or butylgermanium trichloride.

These components (e) can be co-used at any ratio.

The mole ratio of the component (e) to the component (a) is preferably from 0.1 to 100, more preferably from 0.5 to 50. When the mole ratio is less than 0.1, the modification reaction does not proceed sufficiently and, in addition, the improvement effect on wear resistance is insufficient. When the mole ratio
10 exceeds 100, the improvement effect does not increase any further and, in some cases, toluene insolubles (gel) are formed.

The modification reaction is effected at a temperature of preferably 160 °C or less, more preferably 0 ° to 130 °C, for a period of preferably 0.1 to 10 hours, more preferably 0.2 to 5 hours, with stirring.

15 After the completion of the modification reaction, steam is blown into the polymer solution to remove the solvent, or a poor solvent is added to the polymer solution to coagulate the modified polymer. The modified polymer thus recovered is then dried using a hot roll or under reduced pressure to obtain the objective polymer. Alternatively, the solvent can be removed directly from the polymer solution under reduced pressure to obtain the objective polymer.

20 The modified conjugated diene polymer obtained in this invention is of a high cis-1,4 diene polymer. When it is a modified polybutadiene, the cis-1,4 content is 70% or more, preferably 80% or more. When it is a modified polyisoprene, the cis-1,4 content is 88% or more. In the case of a high cis-1,4 butadiene-isoprene copolymer, the cis-1,4 content in the butadiene unit is 80% or more and the cis-1,4 content in the isoprene unit is 88% or more.

25 The proportions of butadiene and isoprene in this copolymer can be varied freely.

The modified conjugated diene polymer obtained in this invention may have a molecular weight varying over a wide range. Its Mooney viscosity ($ML_1 + 1$, 100 °C) is preferably 10 to 120, more preferably 15 to 100 though not critical.

The modified conjugated diene polymer, when it is a copolymer, can be obtained as a block copolymer
30 or a random copolymer depending upon the structure of the reactive polymer.

The structure of the modified conjugated diene polymer of this invention can be confirmed, for example, by infrared absorption spectrum based on absorption due to $Sn-\phi$ bond in the vicinity of 700 cm^{-1} and absorption due to $Sn-CH_3$ in the vicinity of 770 cm^{-1} .

35 When the diphenyltin dichloride is used as the component (e), the structure can be confirmed by the Fourier transform NMR spectrometer (hereinafter referred to as FT-NMR) using tetramethylsilane as the standard substance based on the peak in the vicinity of $\delta = 7.4$ ppm due to $Sn-\phi$ bond.

In case the modifying component is not used, the molecular weight distribution of the resulting polybutadiene can not be determined by GPC using an ultraviolet ray of 254 nm as a detector.

40 However, when a phenyl group-containing compound, for example, is used as the modifying component, the molecular weight distribution of the resulting modified polymer determined by ultraviolet rays and the molecular weight distribution of the polymer determined by differential refractometer can be correlated because of the presence of ultraviolet-ray absorption due to the phenyl group. From this correlation, the presence of the functional group in the modified polymer can be confirmed.

The modified conjugated diene polymer (I) of this invention can be used alone or in blend with 80% by
45 weight or less of natural rubber (II) and/or other rubber (III) such as cis-1,4-polyisoprene, emulsion-polymerized styrene-butadiene copolymer, solution-polymerized styrene-butadiene copolymer, low cis-1,4-polybutadiene, high cis-1,4-polybutadiene, ethylenepropylene-diene copolymer, chloroprene, halogenated butyl rubber or NBR. When it is used in blend, the blending ratio is preferably 20 : 80 to 90 : 10 in terms of weight ratio of (I) : [(II) + (III)]. When the total content of (II) and (III) in the blend exceeds 80% by weight,
50 the effect of this invention cannot be expected. The modified conjugated diene polymer of this invention or its blend can, if necessary, be extended with an aromatic, naphthenic or paraffinic oil and then mixed with conventional compounding agents for vulcanized rubber such as a filler (e.g. carbon black, silica, magnesium carbonate, calcium carbonate, or glass fiber.), stearic acid, zinc white, an antioxidant, a vulcanizing accelerator and a vulcanizing agent, to form a rubber composition.

55 This rubber composition can be molded, vulcanized and then used in various applications such as tire (tread, undertread, carcass, side wall, bead), hose, belt, shoe sole, window frame, sealing material, rubber vibration insulator and other industrial applications.

This invention will be explained in more detail below referring to Examples, which are not by way of limitation but by way of illustration.

In the Examples, parts and % are by weight unless otherwise specified.

Various measurements in the Examples were made according to the following methods.

- 5 The reaction between a reactive polymer obtained by polymerization with a lanthanum series rare earth metal catalyst and a specific halogen compound was confirmed by examining the change of Mooney viscosity before and after the reaction, or by conducting a model reaction using a polymer having a number-average molecular weight of several thousands and subjecting the product to GPC and IR analysis.

10 Mooney viscosity

Measured according to JIS K 6300 (preheating: 1 minute; measurement: 4 minutes; and temperature: 100 °C).

15 Microstructure of polymer

Measured according to the IR absorption spectrum method (the Morero method).

- 20 The modified polymer obtained according to this invention was subjected to kneading with the following compounding recipe using a 230-cm³ Brabender and a 15 2 mm (6-inch) roll, and then the resulting compound was vulcanized at 145 °C for a predetermined period of time to obtain a vulcanizate. The vulcanizate was subjected to various measurements.

Compounding recipe

25

Polymer	100 parts
Carbon black (HAF)	50 parts
Zinc white	3 parts
Stearic acid	2 parts
30 Antioxidant (810 NA ^{*1})	1 part
Vulcanizing accelerator (TP ^{*2})	0.8 part
Vulcanizing accelerator (MSA ^{*3})	1 part
Sulfur	1.5 parts

35

^{*1} N-phenyl-N'-isopropyl-p-phenylenediamine

^{*2} Sodium dibutyldithiocarbamate

^{*3} N-oxydiethylene-2-benzothiazolesulfenamide

40 Tensile characteristics and hardness

Measured according to JIS K 6301.

45 Heat generation

Impact resilience (%) according to the Dunlop impact resilience test was used as a yardstick of heat generation. The measurement was made according to BS 903. A larger impact resilience (%) implies lower heat generation, which is desirable.

50 Abrasion

Measured according to ASTM D 2228 (the Pico method). A large Pico abrasion index implies superior abrasion resistance.

55 Example 1

2.5 kg of cyclohexane and 500 g of 1,3-butadiene were placed in a reactor having an internal volume of 5 liters and equipped with a stirrer, in a nitrogen atmosphere. Separately, a catalyst was previously

prepared by mixing (a) 0.93 mmol of neodymium 2-ethylhexanoate, (b) 27.7 mmol of triethylaluminum, (b) 10.2 mmol of diisobutylaluminum hydride, (c) 2.3 mmol of diethylaluminum chloride and (d) 1.85 mmol of acetylacetone in the presence of 4.6 mmol of 1,3-butadiene and aging the mixture at 40 °C for 30 minutes. This catalyst was added to the contents in the above reactor. The whole mixture was subjected to adiabatic reaction at 70 °C for 1.5 hours. The reaction conversion of 1,3-butadiene was almost 100%. In order to measure the Mooney viscosity of the formed polybutadiene, a part of the polymerization mixture was taken out, coagulated and dried. The drying product (polymer) had a Mooney viscosity of 49.

The polymerization mixture was cooled to 60 °C. Thereto was added (e) 2.33 mmol of diphenyltin dichloride. The mixture was stirred for 30 minutes. Then, 3.0 g of 2,6-di-*t*-butyl-*p*-cresol was added. Steam was blown into the mixture for coagulation. The coagulation product was dried using a hot roll of 100 °C. The modified poly(1,3-butadiene) thus obtained had such a microstructure that the *cis*-1,4 content was 97.3%, the *trans*-1,4 content was 1.3% and the vinyl content was 1.4%. Its Mooney viscosity was 64.

The evaluation results on the properties of the vulcanizate of the above modified poly(1,3-butadiene) are shown in Table 1.

Comparative Examples 1 and 2

Comparative Example 1 is a case where no diphenyltin dichloride was used in Example 1. Comparative Example 2 is a case where a commercially available polybutadiene (BR-01 manufactured by Japan Synthetic Rubber Co., Ltd.) was vulcanized to obtain a vulcanizate. The evaluation results on the properties of the two vulcanizates are shown in Table 1.

As is appreciated from the comparison of Example 1 with Comparative Examples 1 and 2, the modified conjugated diene polymer of this invention obtained by reacting the reactive polymer just after polymerization using the lanthanum series rare earth metal catalyst, with diphenyltin dichloride has remarkably improved abrasion resistance.

Examples 2 to 7

Example 2 is a case where the amount of diphenyltin dichloride used was increased as compared with Example 1. Examples 3 and 7 are cases where triphenyltin chloride was used in place of the diphenyltin dichloride in Example 1. Examples 4 and 5 are cases where phenyltin trichloride was used in place of the diphenyltin dichloride in Example 1. Example 6 is a case where dibutyltin dichloride was used in place of the diphenyltin dichloride in Example 1.

The evaluation results on the properties of each vulcanizate are shown in Table 1.

Comparative Example 3

A poly(1,3-butadiene) was produced in the same manner as in Example 1, except that carbon tetrachloride was used in place of the diphenyltin dichloride. The results of polymerization and the evaluation results on the properties of the vulcanizate are shown in Table 1.

Table 1

	Example 1	Comparative Example 1	Comparative Example 2	Example 2
Type of organometal halide (component (e))	$\phi_2\text{SnCl}_2$	Not used	-	$\phi_2\text{SnCl}_2$
Mole ratio of component (e)/ component (a)	2.5	-	-	5.0
Mooney viscosity before and after addition of component (e)				
Before addition	49	51	(44)	54
After addition	64	-		65
Microstructure (%)				
Cis-1,4 content	97.3	96.6	95.3	96.8
Trans-1,4 content	1.3	1.5	2.1	1.4
Vinyl content	1.4	1.9	2.6	1.8
Properties of vulcanizate				
Tensile characteristics				
200% modulus (kgf/cm ²) [kPa]	106 [10.4]	97 [9.5]	92 [9.0]	112 [11.0]
300% modulus (kgf/cm ²) [kPa]	171 [16.6]	158 [15.5]	140 [13.7]	178 [17.5]
Tensile strength (kgf/cm ²) [kPa]	217 [21.3]	221 [21.7]	192 [18.8]	218 [21.4]
Elongation at break (%)	380	410	390	370
Hardness (JIS A)	73	73	71	75
Dunlop impact resilience (%)				
Room temperature	63	64	59	66
50°C	66	65	60	66
80°C	67	66	63	67
Pico abrasion index ^a	129	107	100	123

Note: ^a In this measurement, the abrasion loss of a vulcanizate of a commercially available polybutadiene JSR BR-01 measured according to the same Pico method was taken as a reference index of 100.

- Cont'd -

Table 1 (Cont'd)

Example 3	Example 4	Example 5	Example 6	Example 7	Comparative Example 3
$\phi_3\text{SnCl}$	ϕSnCl_3	ϕSnCl_3	$(n\text{-Bu})_2\text{SnCl}_2$	$\phi_3\text{SnCl}$	CCl_4
10.0	1.7	3.3	5.0	30	25
77 86	51 52	54 55	48 61	25 48	48 48
96.9 1.3 1.8	97.0 1.3 1.7	97.3 1.4 1.3	96.4 1.7 1.9	96.4 1.8 1.8	96.3 1.7 2.0
115 [11.3] 176 [17.3] 220 [21.6] 370	97 [9.5] 157 [15.4] 205 [20.1] 400	100 [9.8] 162 [15.9] 209 [20.5] 390	115 [11.3] 183 [17.9] 221 [21.7] 380	98 [9.6] 155 [15.2] 201 [19.7] 360	96 [9.4] 159 [15.6] 220 [21.6] 400
75	73	75	74	73	73
67 67 69	63 64 66	65 66 68	67 67 68	66 66 67	63 64 65
120	126	126	127	116	106

Example 8

The modified polymer (polymer A) obtained in accordance with Example 1, having a Mooney viscosity of 57 and having a cis-1,4 content of 97.1%, a trans-1,4 content of 1.5% and a vinyl content of 1.4% was blended with a natural rubber in the blending ratio shown in Table 2. The blend was vulcanized with the compounding recipe shown previously.

The properties of the vulcanizate are shown in Table 2.

Examples 9 to 11 and Comparative Examples 4 and 5.

Vulcanization was conducted in the same manner as in Example 8, except that the polymer A (see Table 3) was replaced by the following polymers B to F (see Table 5). The properties of each vulcanizate are shown in Table 2.

Polymer B: A modified polymer obtained in the same manner as mentioned above for the polymer A, except that triphenyltin chloride was used in place of the diphenyltin dichloride.

Polymer C: A modified polymer obtained in the same manner as mentioned above for the polymer A, except that phenyltin trichloride was used in place of the diphenyltin dichloride.

Polymer D: A modified polymer obtained in the same manner as mentioned above for the polymer A, except that dibutyltin dichloride was used in place of the diphenyltin dichloride.

Polymer E: An unmodified polymer obtained in the same manner as mentioned above for the polymer A, except that no modification with diphenyltin dichloride was conducted.

Polymer F: A polymer obtained in the same manner as mentioned above for the polymer A, except that the diphenyltin dichloride was replaced by carbon tetrachloride.

Comparative Examples 6 and 7

Vulcanization was conducted in the same manner as in Example 8, except that a commercially available polybutadiene rubber (JSR BR 01 manufactured by Japan Synthetic Rubber Co. Ltd) was used in place of the polymer A. The properties of each vulcanizate are shown in Table 2.

From the comparison of Examples 8 and 11, with Comparative Examples 4 to 7, it is clear that the rubber compositions of this invention have excellent wear resistance, good mechanical strengths and low heat generation characteristics.

Comparative Example 8

Vulcanization was conducted in the same manner as in Example 8, except that the blending ratio of the polymer A to the natural rubber was changed to 10:90. The properties of the vulcanizate obtained are shown in Table 2, which indicates that the effect of this invention cannot be expected when the rubber composition contains a too small amount of the polymer A.

Table 2

Type of polymer (parts)	Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6
Polymer A	50	50	50	50
Polymer B				
Polymer C				
Polymer D				
Polymer E				
Polymer F				
JSR-BR01	50	50	50	50
Natural rubber (RSS No. 3)				
Properties of vulcanizate				
Tensile characteristics				
300% modulus (kgf/cm ²) [kPa]				
Tensile strength (kgf/cm ²) [kPa]				
Elongation at break (%)	121 [11.9] 262 [25.7] 520	113 [11.1] 251 [24.6] 530	106 [10.4] 248 [24.3] 490	114 [11.2] 254 [24.9] 500
Hardness (JIS A)	63	63	64	65
Dunlop impact resilience (%)	59 62 63	56 58 60	56 59 61	55 57 59
Room temperature				
50°C				
80°C	125	108	106	100
Pico abrasion index*				

Note: * In this measurement, the abrasion loss of a vulcanizate of a rubber composition [50% by weight of a polybutadiene rubber (JSR-BR01) and 50% by weight of a natural rubber (RSS No. 3)] measured according to the same Pico method was taken as a reference index of 100.

- Cont'd -

Table 2 Cont'd)

Example 9	Example 10	Example 11	Comparative Example 7	Comparative Example 8
30	70	70		10
70	30	30	70 30	90
125 [12.3] 274 [26.9] 480	109 [10.7] 231 [22.7] 520	110 [10.8] 225 [22.1] 510	106 [10.4] 227 [22.3] 490	145 [14.2] 295 [28.9] 450
64	63	64	65	64
54	60	60	59	53
56	63	62	61	54
58	66	65	64	55
118	132	135	105	94

Table 3

	Polymer A	Polymer B	Polymer C	Polymer D	Polymer E	Polymer F
Type of modifying component	$\phi_2\text{SnCl}_2$	$\phi_3\text{SnCl}$	ϕSnCl_3	$(n\text{-Bu})_2\text{SnCl}_2$	Not used	CCl_4
Mole ratio of modifying component/component (a)	2.5	15	5	10	-	30
Mooney viscosity before and after addition of modifying component	43 57	35 42	32 48	28 41	43 -	46 46
Microstructure (%)						
Cis-1,4 content	97.1	97.0	96.8	97.3	96.9	96.8
Trans-1,4 content	1.5	1.6	1.4	1.5	1.4	1.4
Vinyl content	1.4	1.4	1.8	1.2	1.7	1.8

Claims

1. A process for producing a modified conjugated diene polymer which comprises the steps of (i) polymerizing a conjugated diene in an inert solvent in the presence of a catalyst comprising (a) a lanthanum series rare earth metal compound, (b) an organoaluminum compound represented by the

general formula, $A1R^1R^2R^3$ (wherein R^1 , R^2 and R^3 , which may be same or different, are hydrogen atoms or hydrocarbon groups with 1 to 8 carbon atoms and at least one of R^1 , R^2 and R^3 is said hydrocarbon group) and, if necessary, (c) a Lewis acid and/or (d) a Lewis base and (II) modifying the resulting reactive polymer with at least one modifying compound which is:

(e) an organometal halide compound represented by the general formula, R^4MX_{4-n} (wherein R^4 is an alkyl group of 1 to 20 carbon atoms or an aryl group, M is a tin or germanium atom, X is a halogen atom, and n is an integer from 1 to 3).

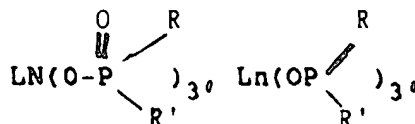
2. A process according to Claim 1, wherein the conjugated diene is 1,3-butadiene, isoprene or a mixture thereof.

3. A process according to Claim 1 or 2 wherein the lanthanum series rare earth element compound (a) is a compound represented by the general formula, LnY_3^2 (wherein Ln is at least one lanthanum series rare earth element having an atomic number of 57 to 71 and Y^2 is a hydrocarbon residue, an alkoxide residue, a thioalkoxide residue, an amide residue, a phosphoric acid salt residue, a phosphorous acid salt residue or a carboxylic acid salt residue).

4. A process according to Claim 3, wherein the Ln is at least one member selected from the group consisting of cerium, praseodymium, neodymium and gadolinium.

5. A process according to Claim 3, wherein the Ln is neodymium.

6. A process according to Claim 3, 4 or 5 wherein the LnY_3^2 compound is a compound represented by the general formula, LnR_3 , $Ln(OR)_3$, $Ln(SR)_3$, $Ln(NR_2)_3$,



LnX_3 or $(RCOO)_3Ln$

(wherein Ln has the same definition as given above, R and R', which may be the same or different, are hydrocarbon groups with 1 to 20 carbon atoms, and X is a halogen atom).

7. A process according to Claim 3, wherein the lanthanum series rare earth element compound (a) is selected from the group consisting of neodymium trichloride, didymium trichloride (the didymium is a rare earth metal mixture consisting of 72% by weight of neodymium, 20% by weight of lanthanum and 8% by weight of praseodymium), neodymium 2-ethylhexanoate, didymium 2-ethylhexanoate, neodymium naphthenate, neodymium 2,2-diethylhexanoate, neodymium trimethacrylate and polymers of neodymium trimethacrylate.

8. A process according to any of Claims 1 to 7 wherein the organoaluminum compound (b) is trimethylaluminum, triethylaluminum, triisopropylaluminum, tributylaluminum, triisobutylaluminum, trihexylaluminum, tricyclohexylaluminum, diisobutylaluminum hydride, diethylaluminum hydride, dipropylaluminum hydride, ethylaluminum dihydride, propylaluminum dihydride or isobutylaluminum dihydride.

9. A process according to any preceding Claim, wherein the mole ratio of the component (b) to the component (a) is from 10:1 to 150:1.

10. A process according to Claim 9, wherein the mole ratio of the component (b) to the component (a) is from 15:1 to 100:1.

11. A process according to any of Claims 1-10, wherein the Lewis acid (c) is selected from the group consisting of aluminum halide compounds represented by the general formula $A1R_m^5X_{3-m}$ (wherein R^5 is a hydrocarbon group having 1 to 8 carbon atoms, m is 0 or a positive number from 1 to 3, and X is a

halogen atom), halogen elements, tin halides and titanium halides.

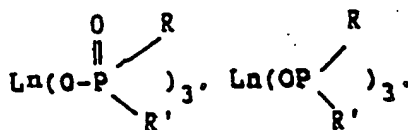
12. A process according to Claim 11, wherein the Lewis acid (c) is selected from the group consisting of dimethylaluminum chloride, diethylaluminum chloride, dibutylaluminum chloride, ethylaluminum sesquichloride, ethylaluminum dichloride, or bromides or iodides corresponding thereto.
13. A process according to any preceding Claim wherein the mole ratio of the component (c) to the component (a) is up to 6:1.
14. A process according to Claim 13, wherein the mole ratio of the component (c) to the component (a) is from 0.5:1 to 5.0:1.
15. A process according to any of Claims 1 to 14, wherein the Lewis base (d) is selected from the group consisting of acetylacetone, tetrahydrofuran, pyridine, N,N-dimethylformamide, thiophene, diphenyl ether, triethylamine, organic phosphorus compounds and mono- or dihydric alcohols.
16. A process according to any preceding Claim wherein the mole ratio of the component (d) to the component (a) is up to 20:1.
17. A process according to Claim 16 wherein the mole ratio of the component (d) to the component (a) is from 1:1 to 15:1.
18. A process according to any preceding Claim, wherein the catalyst consists only of the component (a) and the component (b).
19. A process according to any preceding Claim, wherein the catalyst is prepared previously by mixing the components (a) and (b) and if necessary (c) and/or (d) in the presence or absence of a conjugated diene in a polymerization solvent, subjecting the mixture to reaction and then aging the reaction mixture.
20. A process according to Claim 19, wherein the polymerization solvent is at least one member selected from the group consisting of aromatic hydrocarbons, aliphatic hydrocarbons, alicyclic hydrocarbons and halogenated hydrocarbons.
21. A process according to any one preceding Claim, wherein polymerization in the step (I) is conducted at -20 °C to 150 °C.
22. A process according to any one preceding Claim wherein the monomer concentration in the solvent is 5 to 50% by weight.
23. A process according to any one preceding Claim wherein the modification in the step (II) is conducted at 160 °C or less for 0.1 to 10 hours with stirring.
24. A process according to any one of the preceding claims, wherein the component (e) is an organotin halide compound represented by the general formula,
$$R_n^4 MX_{4-n}$$
 wherein M is tin.
25. A modified conjugated diene polymer obtained according to the process of any one preceding Claim.
26. A modified conjugated diene polymer according to Claim 25 having a Mooney viscosity (ML₁₊₄ 100 °C of 10 to 120.

Patentansprüche

1. Verfahren zur Herstellung von modifizierten Polymeren aus konjugierten Dienen, das folgende Schritte umfaßt:
(I) Polymerisation eines konjugierten Diens in einem inerten Lösungsmittel in Gegenwart eines Katalysators, der enthält:

- (a) eine Verbindung eines Seltenerdmetalls der Lanthanreihe,
 (b) eine Organoaluminiumverbindung der allgemeinen Formel $A1R^1R^2R^3$,
 in der R^1 , R^2 und R^3 , die gleich oder verschieden sein können, Wasserstoffatome oder Kohlenwasserstoffgruppen mit 1 bis 8 C-Atomen darstellen, wobei mindestens einer der Substituenten R^1 , R^2 und R^3 eine Kohlenwasserstoffgruppe ist,
 sowie gegebenenfalls
 (c) eine Lewisäure
 und/oder
 (d) eine Lewisbase
 und
 (II) Modifizierung des resultierenden reaktiven Polymers mit mindestens einer Modifizierungsverbindung (e), die eine Organometallhalogenidverbindung der Formel $R^4_n MX_{4-n}$ darstellt, in der R^4 eine Alkylgruppe mit 1 bis 20 C-Atomen oder eine Arylgruppe, M ein Zinn- oder Germaniumatom, X ein Halogenatom und n 1, 2 oder 3 bedeuten.

2. Verfahren nach Anspruch 1, wobei das konjugierte Dien 1,3-Butadien, Isopren oder ein Gemisch dieser Verbindungen ist.
3. Verfahren nach Anspruch 1 oder 2, wobei die Verbindung des Seltenerdelements der Lanthanreihe (a) eine Verbindung der allgemeinen Formel LnY^2_3 ist,
 in der bedeuten: Ln mindestens ein Seltenerdelement der Lanthanreihe mit einer Ordnungszahl von 57 bis 71 und
 Y^2 einen Kohlenwasserstoffrest, einen Alkoxidrest, einen Thioalkoxidrest, einen Amidrest, einen Rest eines Phosphorsäuresalzes, einen Rest eines Salzes der phosphorigen Säure oder einen Rest eines Carbonsäuresalzes.
4. Verfahren nach Anspruch 3, wobei Ln mindestens ein unter Cer, Praseodym, Neodym und Gadolinium ausgewähltes Element ist.
5. Verfahren nach Anspruch 3, wobei Ln Neodym ist.
6. Verfahren nach Anspruch 3, 4 oder 5, wobei die Verbindung LnY^2_3 eine Verbindung der allgemeinen Formeln LnR_3 , $Ln(OR)_3$, $Ln(SR)_3$, $Ln(NR_2)_3$,

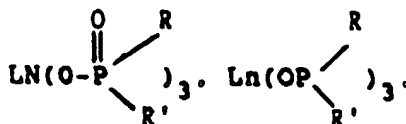


- LnX_3 oder $(RCOO)_3Ln$ ist, worin Ln die gleiche Bedeutung wie oben besitzt und R und R', die gleich oder verschieden sein können, Kohlenwasserstoffgruppen mit 1 bis 20 C-Atomen und X ein Halogenatom bedeuten.
7. Verfahren nach Anspruch 3, wobei die Verbindung des Seltenerdelements der Lanthanreihe (a) ausgewählt ist unter Neodymtrichlorid, Didymiumtrichlorid (wobei Didymium ein Seltenerdmetallgemisch ist, das aus 72 Gew.-% Neodym, 20 Gew.-% Lanthan und 8 Gew.-% Praseodym besteht), Neodym-2-ethylhexanoat, Didymium-2-ethylhexanoat, Neodymnaphthenat, Neodym-2,2-diethylhexanoat, Neodymtrimethacrylat und Polymeren von Neodymtrimethacrylat.
8. Verfahren nach einem der Ansprüche 1 bis 7, wobei die Organoaluminiumverbindung (b) Trimethylaluminium, Triethylaluminium, Triisopropylaluminium, Tributylaluminium, Triisobutylaluminium, Trihexylaluminium, Tricyclohexylaluminium, Diisobutylaluminiumhydrid, Diethylaluminiumhydrid, Dipropylaluminiumhydrid, Ethylaluminiumdihydrid, Propylaluminiumdihydrid oder Isobutylaluminiumdihydrid ist.
9. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Molverhältnis von Komponente (b) zu Komponente (a) 10 : 1 bis 150 : 1 beträgt.

10. Verfahren nach Anspruch 9, wobei das Molverhältnis von Komponente (b) zu Komponente (a) 15 : 1 bis 100 : 1 beträgt.
- 5 11. Verfahren nach einem der Ansprüche 1 bis 10, wobei die Lewisäure (c) ausgewählt ist unter Aluminiumhalogenidverbindungen der allgemeinen Formel $AlR_m^5 X_{3-m}$, worin R^5 eine Kohlenwasserstoffgruppe mit 1 bis 8 C-Atomen, m 0 oder eine positive Zahl von 1 bis 3 und X ein Halogenatom bedeuten, elementaren Halogenen, Zinnhalogeniden und Titanhalogeniden.
- 10 12. Verfahren nach Anspruch 11, wobei die Lewisäure (c) ausgewählt ist unter Dimethylaluminiumchlorid, Diethylaluminiumchlorid, Dibutylaluminiumchlorid, Ethylaluminiumsesquichlorid und Ethylaluminiumdichlorid sowie entsprechenden Bromiden und Jodiden.
13. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Molverhältnis von Komponente (c) zu Komponente (a) bis zu 6 : 1 beträgt.
- 15 14. Verfahren nach Anspruch 13, wobei das Molverhältnis von Komponente (c) zu Komponente (a) 0,5 : 1 bis 5,0 : 1 beträgt.
- 20 15. Verfahren nach einem der Ansprüche 1 bis 14, wobei die Lewisbase (d) ausgewählt ist unter Acetylacetone, Tetrahydrofuran, Pyridin, N,N-Dimethylformamid, Thiophen, Diphenylether, Triethylamin, organischen Phosphorverbindungen und ein- und zweiwertigen Alkoholen.
- 25 16. Verfahren nach einem der vorhergehenden Ansprüche, wobei das Molverhältnis von Komponente (d) zu Komponente (a) bis zu 20 : 1 beträgt.
- 30 17. Verfahren nach Anspruch 16, wobei das Molverhältnis von Komponente (d) zu Komponente (a) 1 : 1 bis 15 : 1 beträgt.
18. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Katalysator lediglich aus Komponente (a) und Komponente (b) besteht.
- 35 19. Verfahren nach einem der vorhergehenden Ansprüche, wobei der Katalysator zuvor durch Mischen der Komponenten (a) und (b) sowie erforderlichenfalls (c) und/oder (d) in Gegenwart oder Abwesenheit eines konjugierten Diens in einem Polymerisationslösungsmittel, Umsetzen des Gemischs und anschließende Alterung des Reaktionsgemischs hergestellt wird.
- 40 20. Verfahren nach Anspruch 19, wobei das Polymerisationslösungsmittel mindestens ein Lösungsmittel ist, das unter aromatischen Kohlenwasserstoffen, aliphatischen Kohlenwasserstoffen, alicyclischen Kohlenwasserstoffen und halogenierten Kohlenwasserstoffen ausgewählt ist.
- 45 21. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Polymerisation in Schritt (I) bei -20 bis 150 °C durchgeführt wird.
22. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Monomerkonzentration im Lösungsmittel 5 bis 50 Gew.-% beträgt.
- 50 23. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Modifizierung in Schritt (II) bei 160 °C oder einer darunterliegenden Temperatur während 0,1 bis 10 h unter Rühren durchgeführt wird.
24. Verfahren nach einem der vorhergehenden Ansprüche, wobei die Komponente (e) eine Organozinnhalogenidverbindung der allgemeinen Formel $R^4 MX_{4-n}$ ist, in der M Zinn bedeutet.
- 55 25. Modifizierte Polymere aus konjugierten Dienen, die nach dem Verfahren nach einem der vorhergehenden Ansprüche erhalten sind.
26. Modifizierte Polymere aus konjugierten Dienen nach Anspruch 25 mit einer Mooney-Viskosität (ML_{1+4} , 100 °C) von 10 bis 120.

Revendications

1. Procédé pour la production d'un polymère diénique conjugué modifié qui comprend les étapes de (I) polymérisation d'un diène conjugué dans un solvant inerte en présence d'un catalyseur comprenant (a) un composé de métal de terre rare de la série du lanthane, (b) un composé d'organoaluminium représenté par la formule générale $AlR^1R^2R^3$ (dans laquelle R^1 , R^2 , R^3 , qui peuvent être identiques ou différents, sont des atomes d'hydrogène ou des groupes d'hydrocarbures avec de 1 à 8 atomes de carbone et au moins un des R^1 , R^2 et R^3 est un tel groupe d'hydrocarbure) et, si nécessaire, (c) un acide de Lewis et/ou (d) une base de Lewis et (II) modification du polymère réactionnel résultant avec au moins un composé modificateur qui est:
 - (e) un composé halogénure organométallique représenté par la formule générale $R_n^4 MX_{4-n}$ (dans laquelle R^4 est un groupe alkyle de 1 à 20 atomes de carbone ou un groupe aryle, M est un atome d'étain ou de germanium, X est un atome d'halogène et n est un nombre entier de 1 à 3).
2. Procédé selon la revendication 1, dans lequel le diène conjugué est le 1,3-butadiène, l'isoprène ou un de leurs mélanges.
3. Procédé selon la revendication 1 ou 2, dans lequel le composé d'élément de terre rare de la série du lanthane (a) est un composé représenté par la formule générale LnY_3^2 (dans laquelle Ln est au moins un élément de terre rare de la série du lanthane ayant un nombre atomique de 57 à 71 et Y^2 est un reste d'hydrocarbure, un reste d'alcoxyde, un reste de thioalcoxyde, un reste d'amide, un reste de sel de l'acide phosphorique, un reste de sel de l'acide phosphoreux ou un reste de sel d'un acide carboxylique).
4. Procédé selon la revendication 3, dans lequel le Ln est au moins un membre choisi dans le groupe constitué par le cérium, le praséodyme, le néodyme et le gadolinium.
5. Procédé selon la revendication 3, dans lequel Ln est le néodyme.
6. Procédé selon la revendication 3, 4 ou 5, dans lequel le composé LnY_3^2 est un composé représenté par la formule générale LnR_3 , $Ln(OR)_3$, $Ln(SR)_3$, $Ln(NR_2)_3$,



7. Procédé selon la revendication 3, dans lequel le composé d'élément de terre rare de la série du lanthane (a) est choisi dans le groupe constitué par le trichlorure de néodyme, le trichlorure de didymium (le didymium est un mélange de métaux de terres rares constitué de 72% en poids de néodyme, de 20% en poids de lanthane et de 8% en poids de praséodyme), le 2-éthylhexanoate de néodyme, le 2-éthylhexanoate de didymium, le naphténate de néodyme, le 2,2-diéthylhexanoate de néodyme, le triméthacrylate de néodyme et les polymères de triméthacrylate de néodyme.
8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel le composé d'organoaluminium (b) est le triméthylaluminium, le triéthylaluminium, le triisopropylaluminium, le tributylaluminium, le triisobutylaluminium, le trihexylaluminium, le tricyclohexylaluminium, l'hydrure de diisobutylaluminium, l'hydrure de diéthylaluminium, l'hydrure de dipropylaluminium, le di-hydrure d'éthylaluminium, le di-hydrure de propylaluminium ou le di-hydrure d'isobutylaluminium.
9. Procédé selon l'une quelconque des revendications précédentes, dans lequel le rapport molaire du composant (b) sur le composant (a) est de 10:1 à 150:1.

10. Procédé selon la revendication 9, dans lequel le rapport molaire du composant (b) sur le composant (a) est de 15:1 à 100:1.
- 5 11. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel l'acide de Lewis (c) est choisi dans le groupe constitué par les composés d'halogénures d'aluminium représentés par la formule générale $AlR_m^5 X_{3-m}$ (dans laquelle R^5 est un groupe d'hydrocarbure ayant de 1 à 8 atomes de carbone, m est 0 ou un nombre positif de 1 à 3 et X est un atome d'halogène), les éléments halogènes, les halogénures d'étain et les halogénures de titane.
- 10 12. Procédé selon la revendication 11, dans lequel l'acide de Lewis (c) est choisi dans le groupe constitué par le chlorure de diméthylaluminium, le chlorure de diéthylaluminium, le chlorure de dibutylaluminium, le sesquichlorure d'éthylaluminium, le di-chlorure d'éthylaluminium ou les bromures ou iodures qui y correspondent.
- 15 13. Procédé selon l'une quelconque des revendications précédentes, dans lequel le rapport molaire du composant (c) sur le composant (a) va jusqu'à 6:1.
14. Procédé selon la revendication 13, dans lequel le rapport molaire du composant (c) sur le composant (a) est de 0,5:1 à 5,0:1.
- 20 15. Procédé selon l'une quelconque des revendications 1 à 14, dans lequel la base de Lewis (d) est choisie dans le groupe constitué par l'acétylacétone, le tétrahydrofurane, la pyridine, la N,N-diméthylformamide, le thiophène, l'éther diphenylique, la triéthylamine, les composés organiques du phosphore et les monoalcools ou les dialcools.
- 25 16. Procédé selon l'une quelconque des revendications précédentes, dans lequel le rapport molaire du composant (d) sur le composant (a) va jusqu'à 20:1.
17. Procédé selon la revendication 16, dans lequel le rapport molaire du composant (d) sur le composant (a) est de 1:1 à 15:1.
- 30 18. Procédé selon l'une quelconque des revendications précédentes, dans lequel le catalyseur est constitué uniquement du composant (a) et du composant (b).
- 35 19. Procédé selon l'une quelconque des revendications précédentes, dans lequel le catalyseur est préparé préalablement en mélangeant les composants (a) et (b) et, si nécessaire (c) et/ou (d) en présence ou en absence d'un diène conjugué dans un solvant de polymérisation, en soumettant le mélange à une réaction et en vieillissant ensuite le mélange réactionnel.
- 40 20. Procédé selon la revendication 19, dans lequel le solvant de polymérisation est au moins un membre choisi dans le groupe constitué par les hydrocarbures aromatiques, les hydrocarbures aliphatiques, les hydrocarbures alicycliques et les hydrocarbure halogénés.
- 45 21. Procédé selon l'une quelconque des revendications précédentes, dans lequel la polymérisation dans l'étape (I) est effectuée à une température de -20 °C à 150 °C.
22. Procédé selon l'une quelconque des revendications précédentes, dans lequel la concentration du monomère dans le solvant est de 5 à 50% en poids.
- 50 23. Procédé selon l'une quelconque des revendications précédentes, dans lequel la modification dans l'étape (II) est effectuée à 160 °C ou à moins de 160 °C pendant de 0,1 à 10 heures sous agitation.
24. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composé (e) est un composé d'halogénure organo-étain représenté par la formule générale $R_n^4 MX_{4-n}$ dans laquelle M est de l'étain.
- 55 25. Un polymère diénique conjugué modifié obtenu selon le procédé de l'une quelconque des revendications précédentes.

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26. Un polymère diénique conjugué modifié selon la revendication 25 ayant une viscosité Mooney (ML₁ ++, 100 °C) de 10 à 120.

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FIG. 1

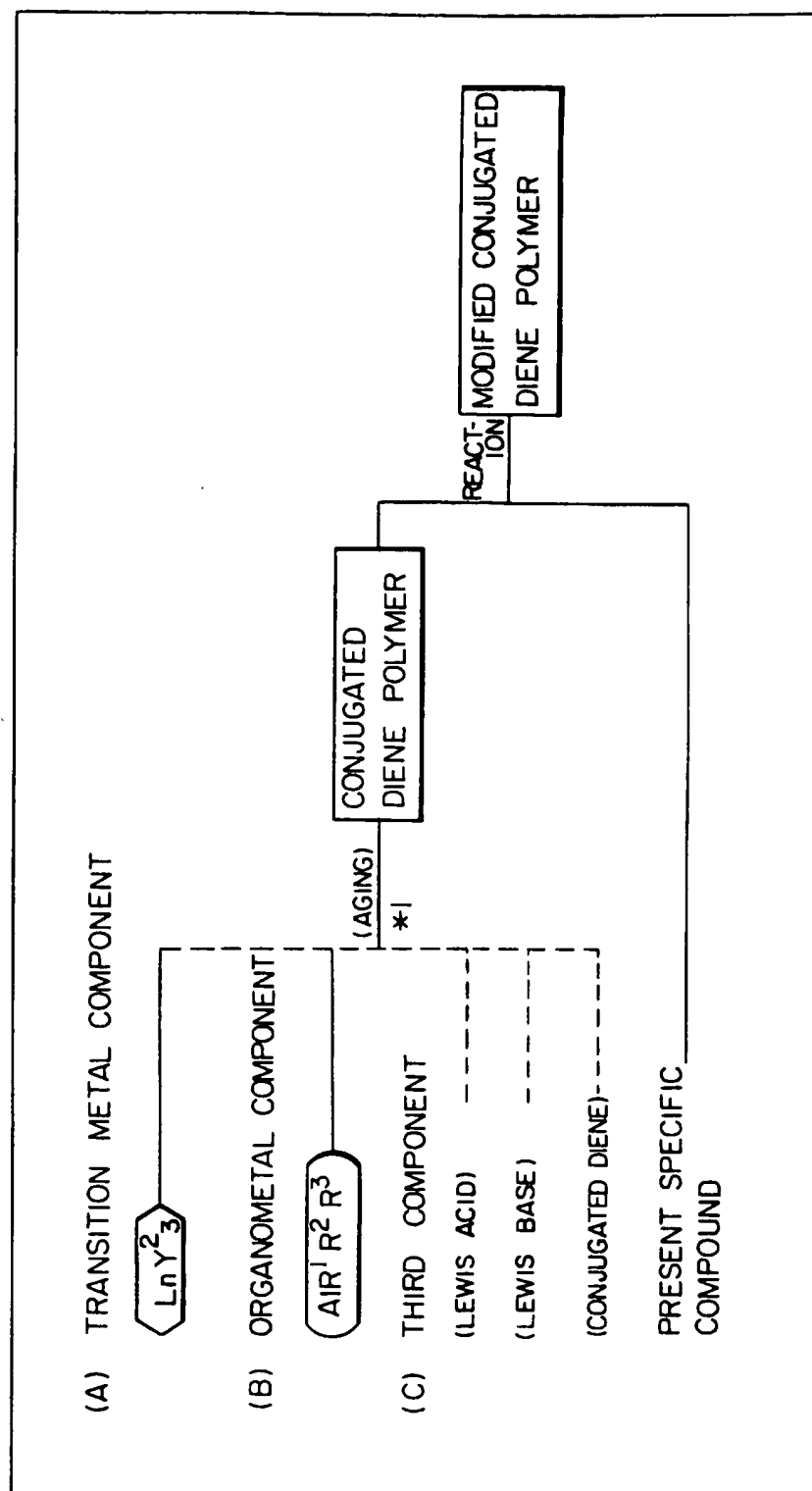


FIG. 2
GPC CHART (EX. 8)

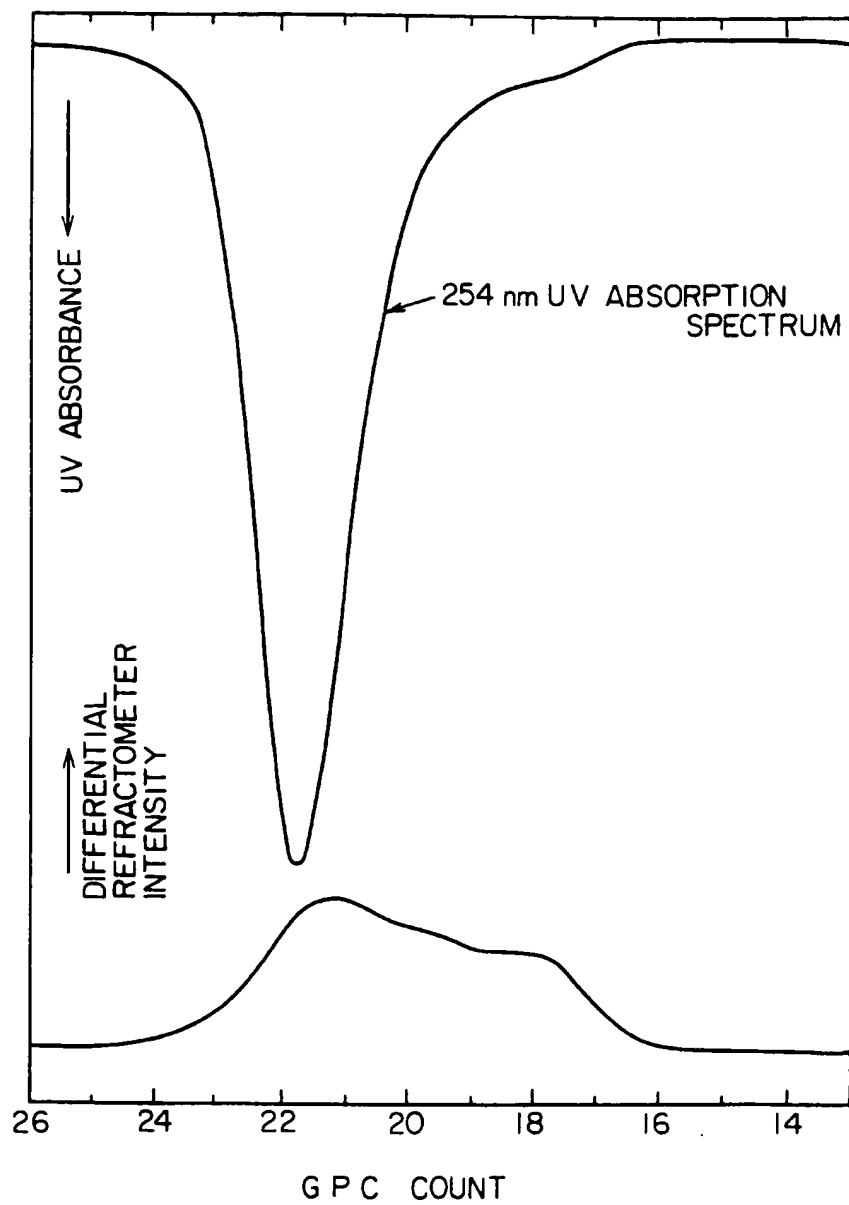


FIG. 3 INFRARED ABSORPTION SPECTRUM (EX. 8)

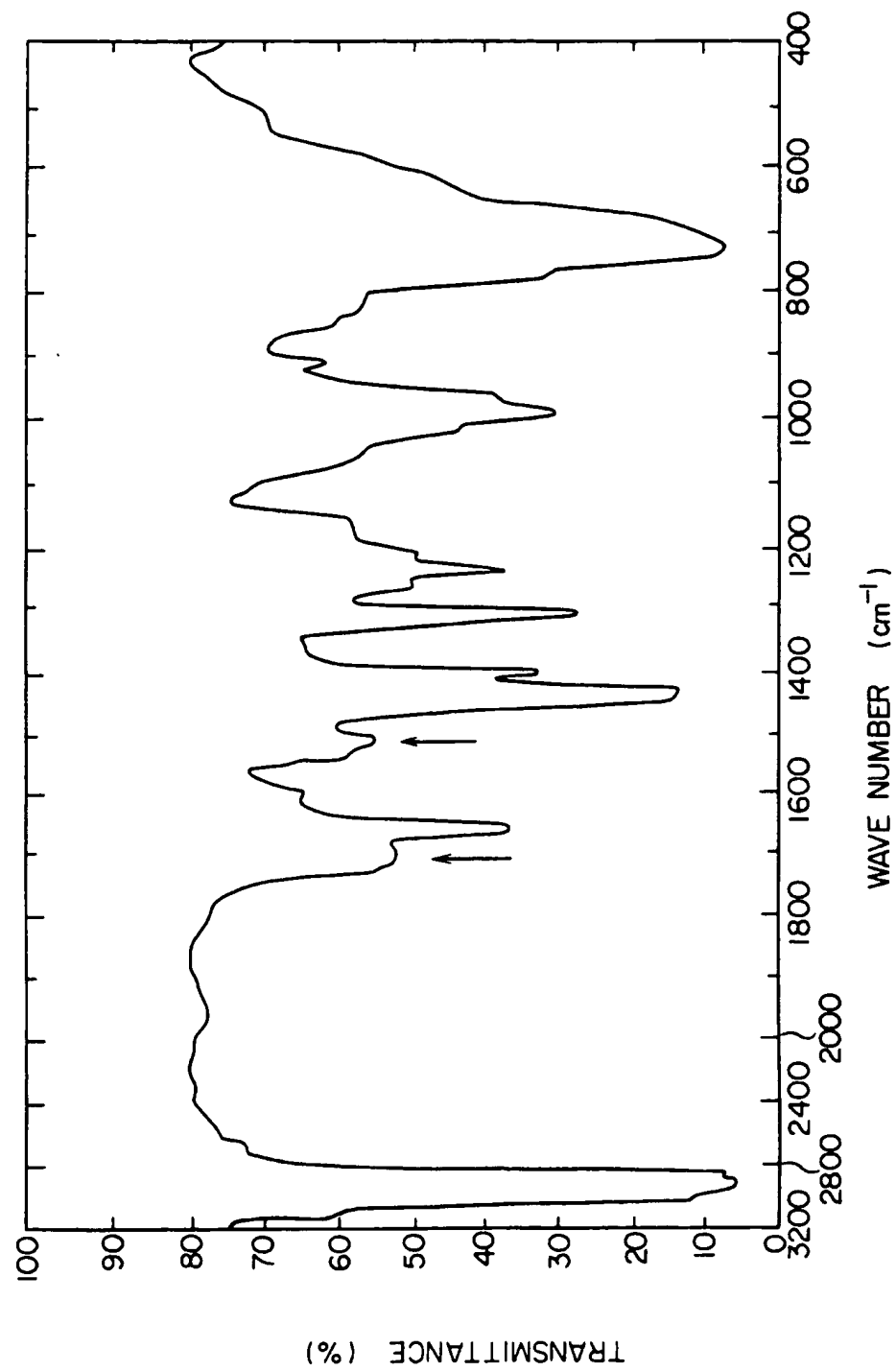


FIG. 4

GPC CHART (COMP. EX. 4)

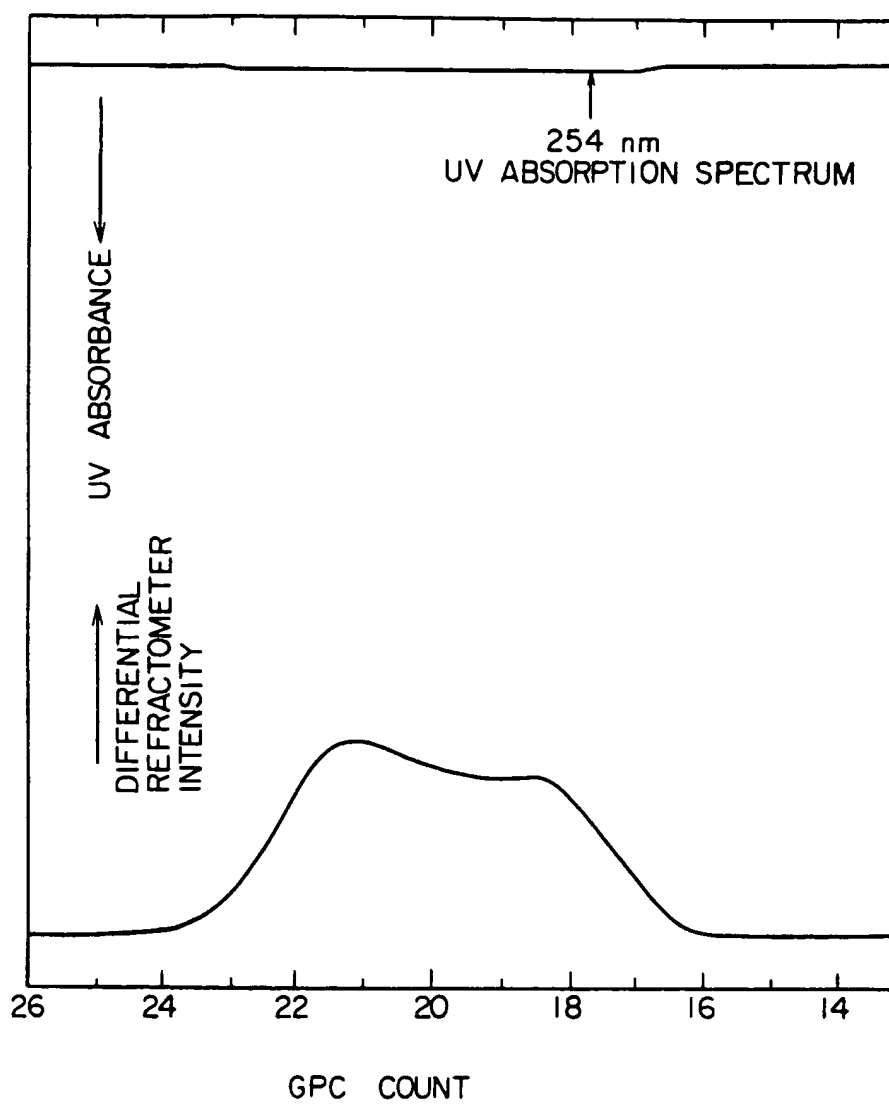


FIG. 5 INFRARED ABSORPTION (COMP. EX. 4)

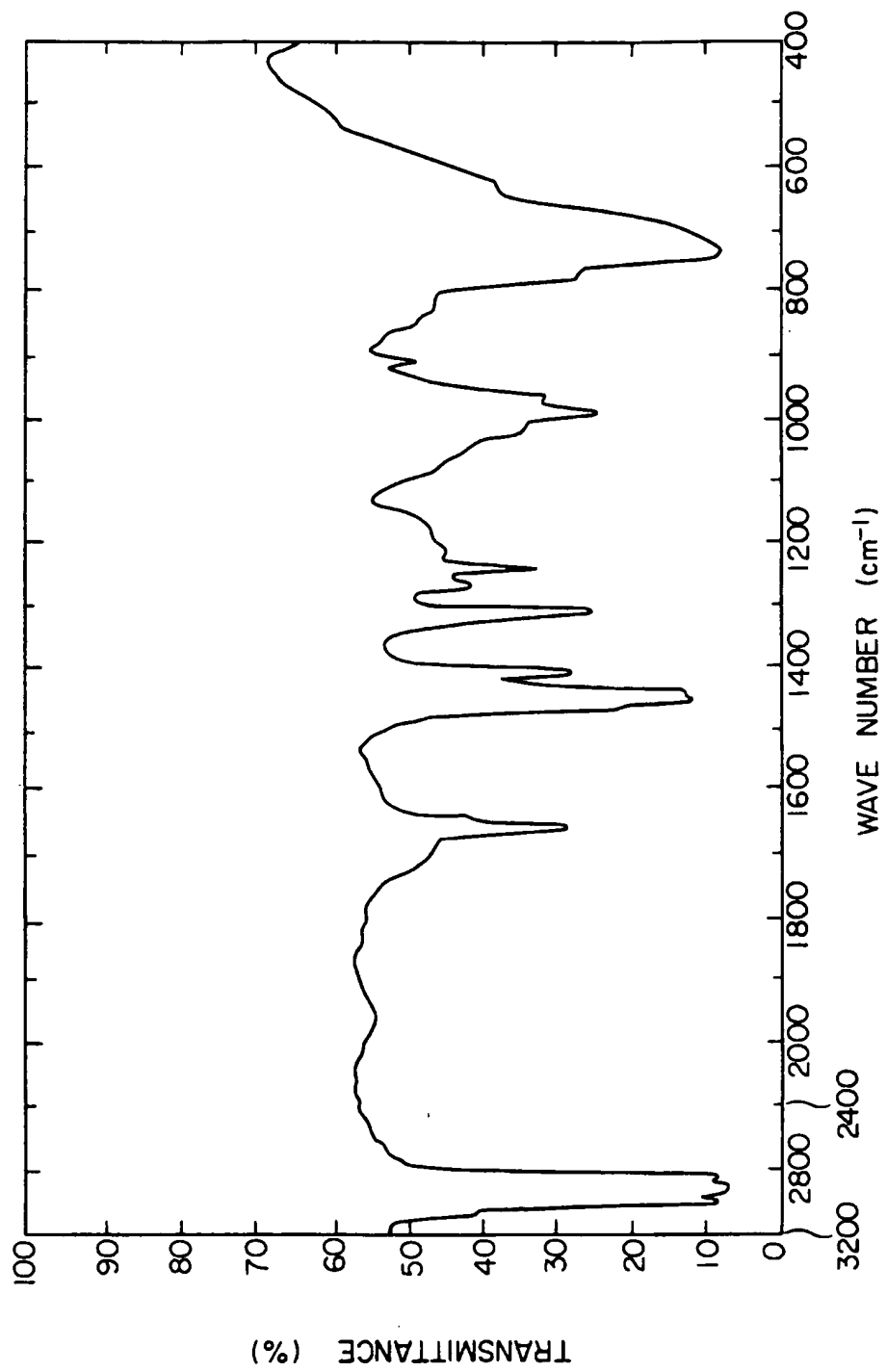


FIG. 6

GPC CHART (EX. 9)

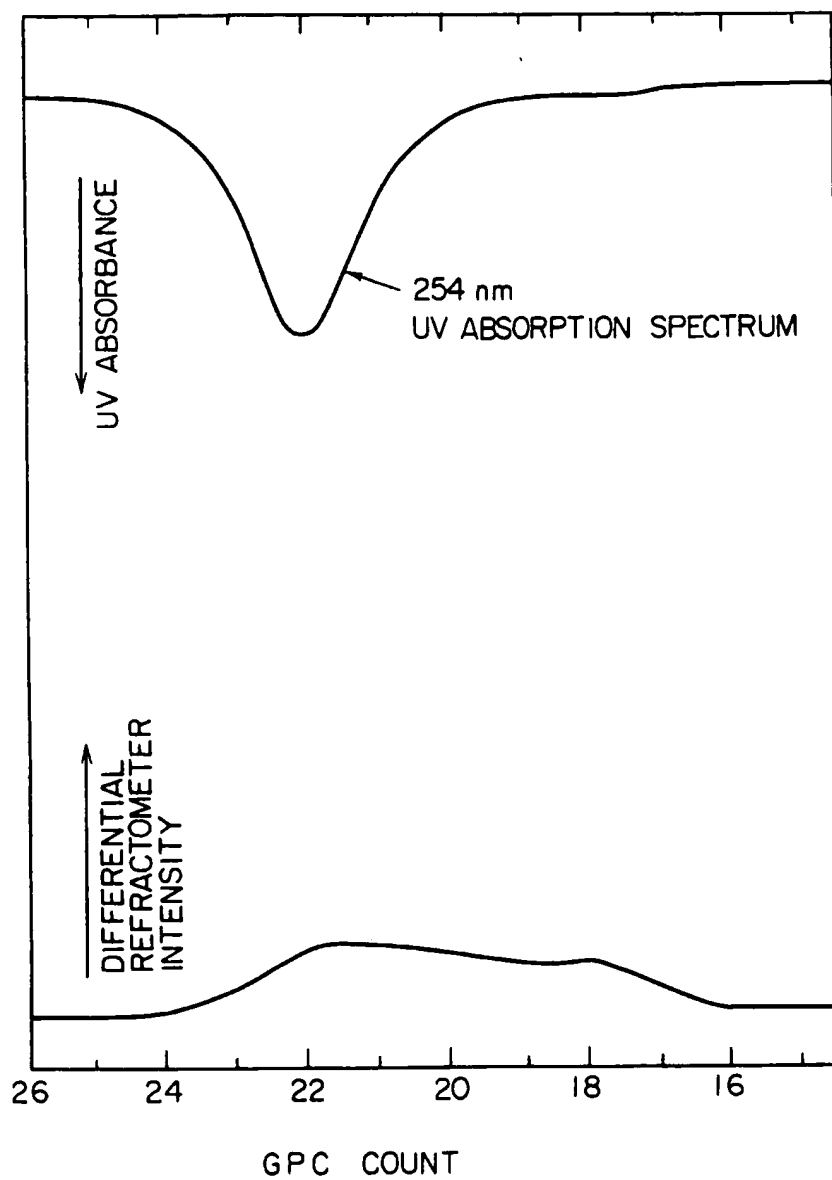


FIG. 7

GPC CHART (EX. 11)

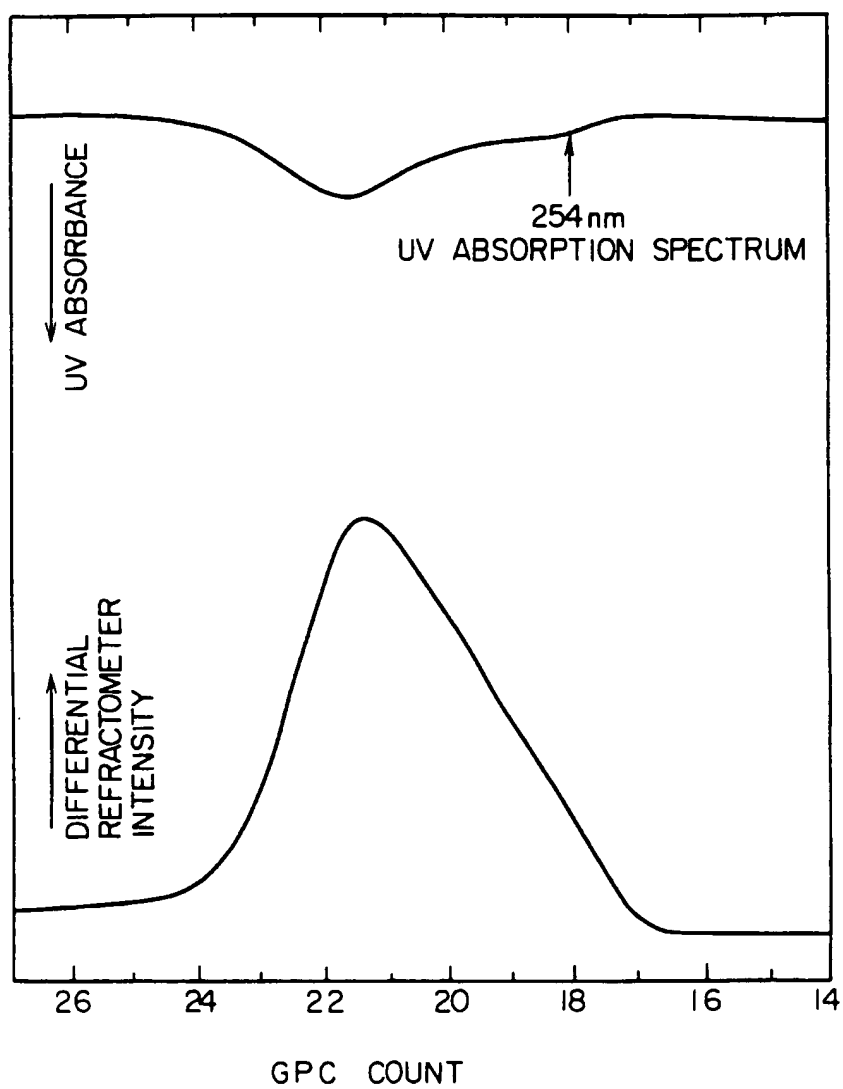


FIG. 8

GPC CHART (EX. 13)

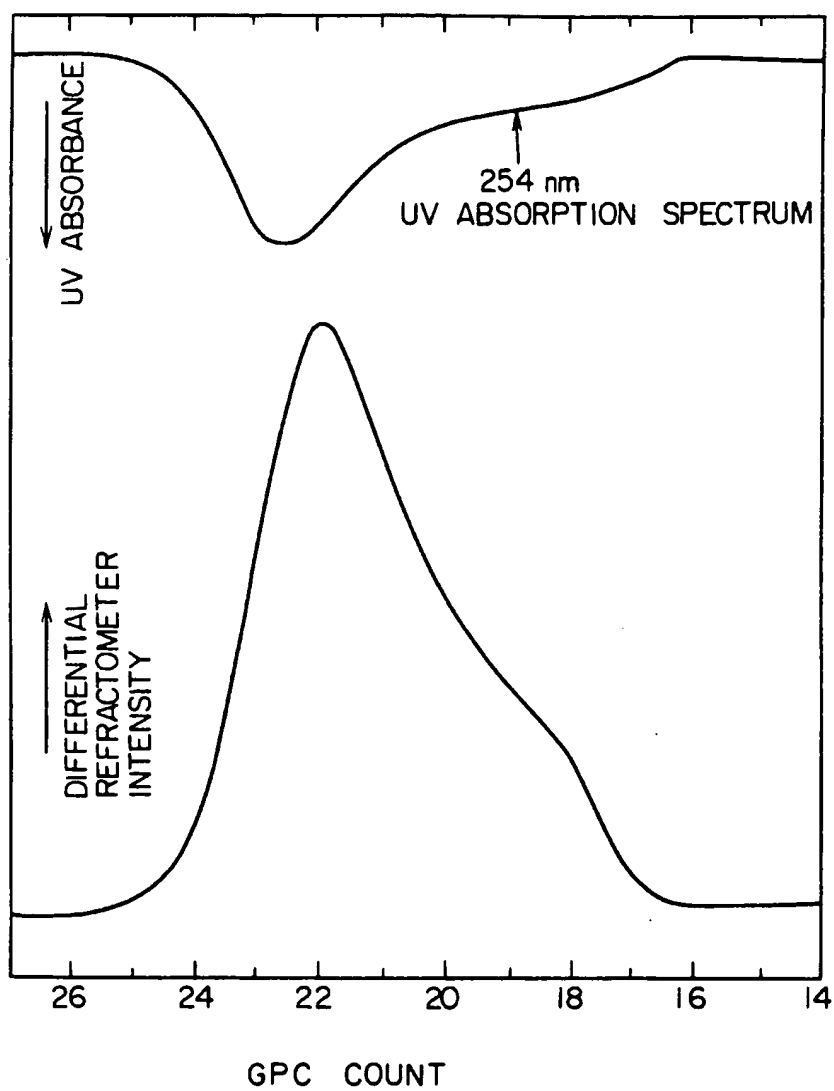


FIG. 9

GPC CHART (EX. 15)

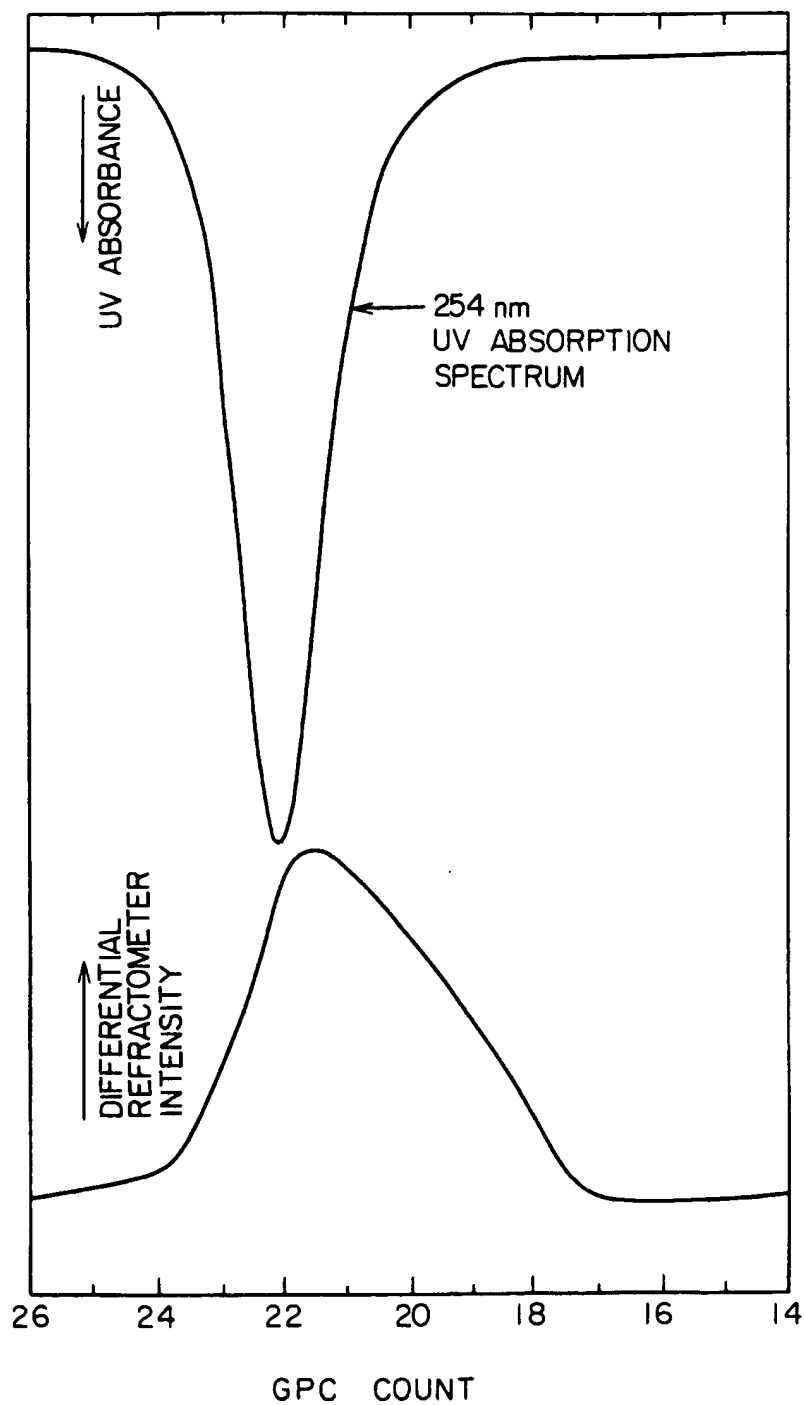


FIG. 10 INFRARED ABSORPTION SPECTRUM (EX. 15)

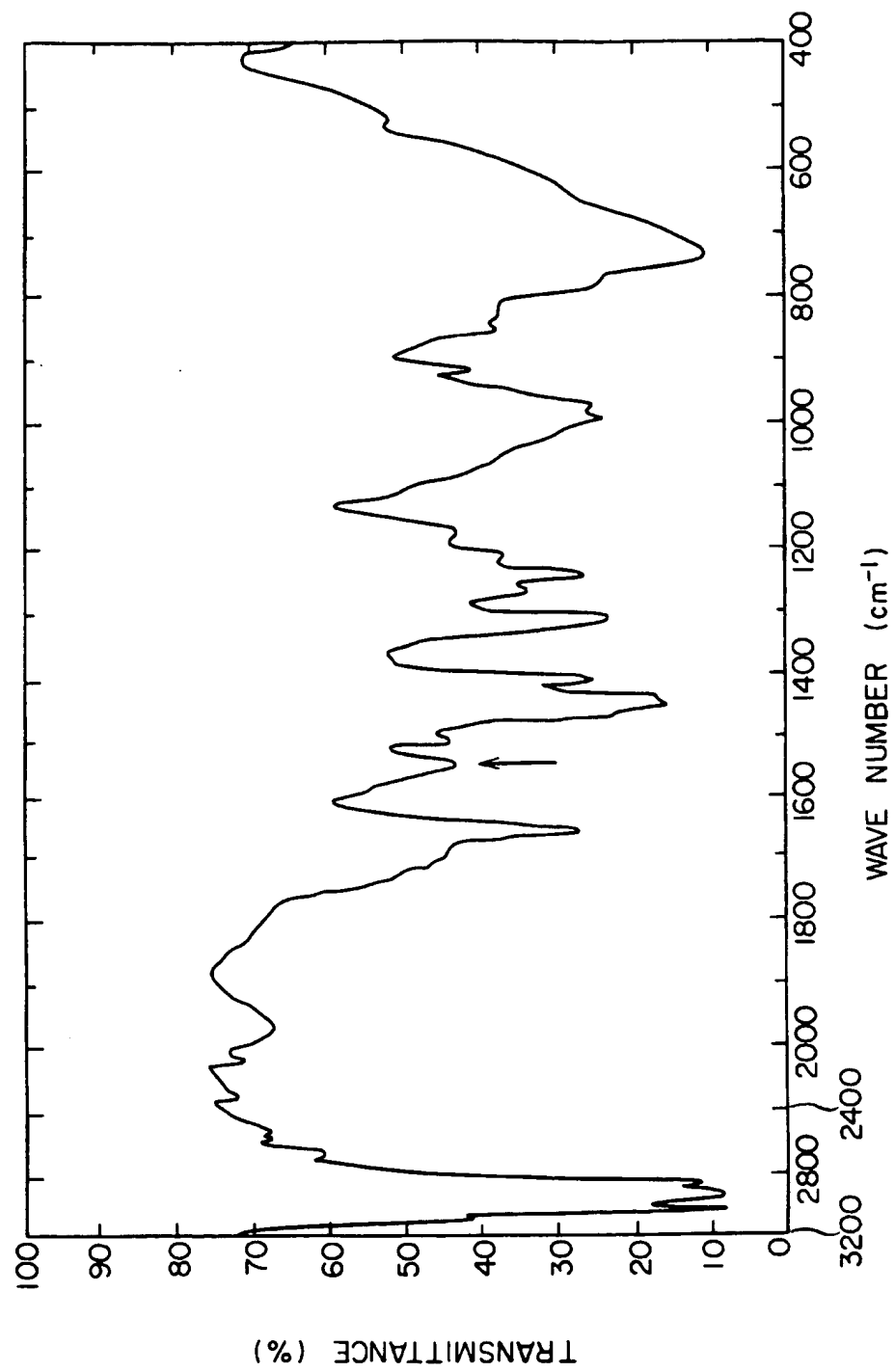


FIG. 11

GPC CHART (EX. 16)

